

## PATENT ABSTRACTS OF JAPAN

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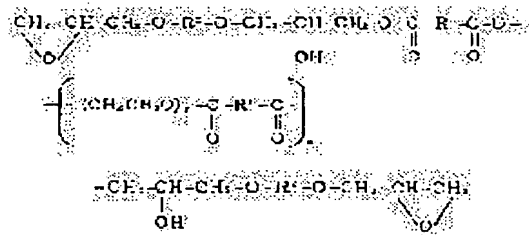
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## (54) EPOXY RESIN AND ITS PRODUCTION

## (57)Abstract:

**PURPOSE:** To obtain an epoxy resin which can be made into a water-base soln. or dispersion and forms a water-resistant coating film when cured with a curative such as a polyamideamine by reacting a polyester resin having a specified number of carboxyl groups in the molecule. with an epoxy resin having a specified number of epoxy groups in the molecule.

**CONSTITUTION:** An epoxy resin of the formula [wherein R1 is a 2-10C linear, branched, or cyclic dicarboxylic acid residue; R2 is-C6H4C(R3)2C6H4-(wherein R3 is H or methyl); n is 20-500; and m is 1 or 2] having a mol.wt. of 1,500-50,000 is obtd. by reacting a polyester resin having at least two carboxyl groups in the molecule and formed by reacting a polyhydric alcohol having a polyoxyethylene chain in the molecule (e.g. polyethylene glycol) with a polycarboxylic acid (e.g. maleic acid) or its anhydride with an epoxy resin having at least two epoxy groups in the molecule (e.g. one obtd. by reacting bisphenol A with epichlorohydrin).



## LEGAL STATUS

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## CLAIMS

[Claim 1] The epoxy resin of the molecular weight 1500–50000 expressed with the following structure expression.

$$\begin{array}{c} \text{CH}_2-\text{CH}-\text{CH}_2-\text{O}-\text{R}^2-\text{O}-\text{CH}_2-\underset{\text{OH}}{\text{CH}}-\text{CH}_2-\text{O}-\overset{\text{O}}{\parallel}\text{C}-\text{R}^1-\overset{\text{O}}{\parallel}\text{C}-\text{O}- \\ \diagdown \quad \diagup \\ \text{O} \end{array}$$
$$\left[ (\text{CH}_2\text{CH}_2\text{O})_n - \overset{\text{O}}{\parallel}\text{C}-\text{R}^1-\overset{\text{O}}{\parallel}\text{C} \right]_m$$
$$-\text{CH}_2-\underset{\text{OH}}{\text{CH}}-\text{CH}_2-\text{O}-\text{R}^2-\text{O}-\text{CH}_2-\text{CH}-\text{CH}_2-$$
$$\diagup \quad \diagdown \\ \text{O}$$

R1 expresses the straight chain of carbon numbers 2-10, branching, or an annular carboxylic acid among [type. Moreover, R2 shows C6H4C(R3)2C6H4. R3 shows H or CH3 here.]

[Claim 2] The epoxy resin according to claim 1 characterized by n being 20–500.

[Claim 3] The epoxy resin according to claim 1 or 2 characterized by m being 1 or 2.

[Claim 4] The manufacture approach of the epoxy resin of the molecular weight 1500-50000 by which it is making [ react ]-polyester resin [ which has two or more carboxyl groups in the intramolecular which the polyhydric alcohol which has a polyoxyethylene chain, a multiple-valued carboxylic acid or its acid anhydride is made to react to intramolecular, and is obtained ], and epoxy resin which has two or more epoxy groups in intramolecular characterized.

[Claim 5] The manufacture approach according to claim 4 characterized by using 1.5–2.2Eq of multiple-valued carboxylic acids to 1Eq of hydroxyl groups of polyhydric alcohol.

[Translation done.]

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DETAILED DESCRIPTION

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[Detailed Description of the Invention]

[0001]

[Industrial Application] This invention offers the new epoxy resin used in the coating field, the adhesives field, etc.

[0002]

[Description of the Prior Art] An epoxy resin is resin which usually contains in intramolecular the compound which has two or more epoxy groups, and is used combining various kinds of curing agents.

[0003] In this case, an epoxy resin gives the hardened material which was [ adhesion / a water resisting property ] excellent by the crosslinking reaction of an epoxy group and a curing agent, or the crosslinking reaction between epoxy groups. Since it is such, the epoxy resin is widely used in the coating and the adhesives field. On the other hand, in the field of a coating and adhesives, the aquosity-ized system attracts attention from the handiness of coating or an adhesion technique further from the work environment side.

[0004] Although the epoxy resin obtained at the reaction of bisphenol A and epichlorohydrin is mainly used in the field of a coating and adhesives, this epoxy resin is insoluble in water.

[0005] Therefore, it was common to have used conventionally amine system curing agents, such as a denaturation amine which created the epoxy resin emulsion which added the surface active agent to the epoxy resin, and carried out emulsification distribution, and gave this epoxy adduct as a curing agent at polyamide polyamine, aromatic amine, or this, in the aquosity-ized system which uses an epoxy resin, aquosity-izing it.

[0006] Thus, it is indicated by JP,49-34734,B, JP,51-33825,B, JP,52-787,B, etc. as a technique made into an epoxy resin emulsion using a surface active agent.

[0007] However, each epoxy resin emulsion indicated by the above-mentioned official report has a bad water resisting property, and the application of use is limited. That is, after film formation, when it uses together with a polyamide amine and coating is carried out, if waterdrop is dropped on a paint film, the part will milk, marks will remain and a finery paint film will not be obtained. This is considered because it exists in the condition of having distributed without the surfactant of a hydrophilic property hardening in a paint film.

[0008] Moreover, it is indicated by JP,60-31853,B as a technique which introduces a hydrophilic component into an epoxy resin. This technique emulsifies an epoxy resin using the epoxy resin resultant which a mean molecular weight 4000, or the polyethylene glycol and epoxy resin of 6000 are made to react under existence of a etherification catalyst by 1/1 equivalent ratio of a hydroxyl group/epoxy group, and is acquired. Although a water resisting property improves considerably compared with the case where an above-mentioned surfactant is used, it is not yet enough.

[0009] The weight per epoxy equivalent of the epoxy resin resultant acquired becomes 150000 or more, and this reason is presumed because bridge formation with a curing agent is inadequate on the occasion of hardening.

[0010]

[Problem(s) to be Solved by the Invention] Aquosity-izing is possible and this invention aims at offering the new epoxy resin which is excellent in a water resisting property, and its manufacture approach.

[0011]

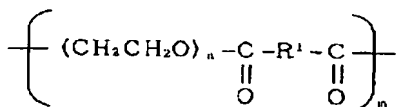
[Means for Solving the Problem] By making the carboxyl group of polyester resin and the epoxy group of an epoxy resin which have two or more carboxyl groups react to the intramolecular which the polyhydric alcohol which has a polyoxyethylene chain, a multiple-valued carboxylic acid, or its acid anhydride is made to react to intramolecular as a result of repeating research wholeheartedly, in order to solve the above-mentioned technical problem, and is obtained, this invention person discovers that the epoxy resin which is excellent in a water

[0012] That is, this invention relates to the manufacture approach of the epoxy resin of the molecular weight 1500-50000 by which it is making [ react ]-polyester resin [ which has two or more carboxyl groups in the intramolecular which the polyhydric alcohol which has a polyoxyethylene chain, a multiple-valued carboxylic acid, or its acid anhydride is made to react to the epoxy resin of the molecular weight 1500-50000 expressed with the following structure expression, and intramolecular, and is obtained ], and epoxy resin which has two or more epoxy groups in intramolecular characterized.

$$\begin{array}{c} \text{CH}_2-\text{CH}-\text{CH}_2-\text{O}-\text{R}^2-\text{O}-\text{CH}_2-\text{CH}-\text{CH}_2-\text{O}-\text{C}(=\text{O})-\text{R}^1-\text{C}(=\text{O})-\text{O}- \\ | \qquad \qquad | \qquad \qquad \qquad \qquad | \qquad \qquad \qquad \qquad || \qquad \qquad || \\ \text{O} \qquad \qquad \text{OH} \qquad \qquad \qquad \qquad \text{O} \qquad \qquad \text{O} \end{array}$$
  
$$\left[ (\text{CH}_2\text{CH}_2\text{O})_n - \text{C}(=\text{O})-\text{R}^1-\text{C}(=\text{O}) \right]_m$$
  
$$-\text{CH}_2-\underset{\text{OH}}{\text{CH}}-\text{CH}_2-\text{O}-\text{R}^2-\text{O}-\text{CH}_2-\text{CH}-\text{CH}_2-$$

[0015] Although R1 in the structure expression of this invention shows the residue of the carboxylic acid of carbon numbers 2-10, it does not ask a straight chain, branching, or how annular. As a multiple-valued carboxylic acid or its acid anhydride, an amber acid, a maleic acid, boletic acid, an adipic acid, sebacic acid, isophthalic acid, terephthalic acid, hexahydrophthalic acid, methyl hexahydrophthalic acid, a tetrahydrophthalic acid, methyl TEORA hydrophthalic acid and a methylene tetrahydrophthalic acid, methyl, a methylene tetrahydrophthalic acid, its acid anhydride, etc. are mentioned, for example.

[Formula 3]



[0020] The epoxy resin of this invention can be obtained by the following manufacture approach. That is, the epoxy resin of this invention can be obtained by making two or more epoxy resins react to the polyester resin and intramolecular which have two or more carboxyl groups in the intramolecular which the polyhydric alcohol which has a polyoxyethylene chain, a multiple-valued carboxylic acid, or its acid anhydride is made to react to intramolecular (henceforth the first process), and is obtained (henceforth the second process).

[0021] The typical thing of polyhydric alcohol which has a polyoxyethylene chain in intramolecular is a polyethylene glycol, and the several n repeat of the oxyethylene chain of a repeat unit has the desirable thing of 20-500.

[0022] A multiple-valued carboxylic acid or its acid anhydride does not ask a straight chain, branching, or how annular. As a multiple-valued carboxylic acid, a maleic acid, hexahydrophthalic acid, an amber acid, boletic acid, an adipic acid, sebacic acid, isophthalic acid, terephthalic acid, methyl hexahydrophthalic acid, a tetrahydrophthalic acid, methyl TEORA hydrophthalic acid and a methylene tetrahydrophthalic acid, methyl, a methylene tetrahydrophthalic acid, its acid anhydride, etc. are mentioned, for example.

[0023] The epoxy resin known from the former which bisphenol A, or Bisphenol F and epichlorohydrin are made to react to intramolecular with the epoxy resin which has two or more epoxy groups, and is obtained is mentioned.

[0024] It is desirable to make the carboxyl group of a multiple-valued carboxylic acid into 1.5-2.2Eq to 1Eq of the hydroxyl group of polyhydric alcohol at the reaction of the first process which obtains polyester resin from polyhydric alcohol, a multiple-valued carboxylic acid, or its acid anhydride, in using a multiple-valued carboxylic acid as an acid component. In using an acid anhydride as an acid component, one acid-anhydride radical is equivalent to two carboxyl groups.

[0025] When a carboxyl group is smaller than 1.5Eq, since the epoxy resin obtained macromolecule-izes beyond the need and the viscosity of a system rises, it is not desirable. Moreover, when larger than 2.2Eq, since the rate of an end epoxy group decreases in the second process, it is not desirable.

[0026] In the case of the usual esterification reaction, the reaction condition of the first process applies correspondingly. Reaction temperature is 250 degrees C or less, and when using a multiple-valued carboxylic acid as an acid component, as for a reaction catalyst, it is desirable to use an acid catalyst or an alkaline catalyst if needed. If an acid anhydride is used as an acid component, at the low temperature around 100 degrees C, it is possible to make it react by use of a non-catalyst or the catalyst of a minute amount, and macromolecule quantification can also be further prevented in this case.

[0027] The reaction of the second process of the polyester resin which has a carboxyl group in intramolecular, and the epoxy resin which has two or more epoxy groups in intramolecular needs to make 1Eq or more of the epoxy group of an epoxy resin react to 1Eq of the carboxyl group of polyester resin. In order to prevent macromolecule quantification of the epoxy resin of this invention, it is desirable to make into 1.5Eq or more the epoxy group of an epoxy resin which has two or more epoxy groups in the above-mentioned intramolecular.

[0028] The reaction temperature of the second process has 100 degrees C - desirable 150 degrees C, and it is desirable to use an alkali catalyst on the occasion of a reaction. As an alkali catalyst, amine compounds, such as hydroxides, such as a sodium hydroxide and a potassium hydroxide, triethylamine, 2-ethyl-4-methylimidazole, and benzyl dimethylamine, or triphenyl phosphine can be mentioned, for example.

[0029] The epoxy resin of this invention is water solubility, and since the hardening paint film which uses together with a curing agent, hardens and is obtained is excellent in a water resisting property, it can be used for constituents for covering, such as various coatings and adhesives.

[0030]

[Example] Although an example is given and this invention is explained hereafter, this invention is not limited to these examples. In addition, the "section" in an example shows the weight section.

[0031] The polyethylene-glycol 43.1 section of a mean molecular weight 3000, the polyethylene-glycol 56.1 section of a mean molecular weight 8000, and the maleic-anhydride 4.2 section were added to the 4 Thu openings flask of 1L equipped with example 1 thermometer, the capacitor, and the agitator, it heated at 120 degrees C, the reaction was continued for 3 hours, and the polyester resin which has two or more carboxyl groups in a molecule was obtained. Subsequently, the triphenyl phosphine 0.2 section was added as the bisphenol A mold epoxy resin 20.9 section with weight per epoxy equivalent 190, and a catalyst, the reaction was performed at 120 degrees C for 4 hours, and the resultant was taken out.

[0032] The equivalent ratio of a polyethylene glycol / maleic anhydride / epoxy resin is 1/2/2.6. The infrared absorption spectrum of a product and <sup>13</sup>C-NMR analysis were performed, and structural analysis was performed. In the infrared absorption spectrum, when characteristic absorption was in 1720cm<sup>-1</sup>, existence of ester has been checked. In NMR, existence of the ester of a polyethylene glycol and a maleic acid has been checked by absorption (64 ppm and 68 ppm). Existence of the ester of an epoxy resin and a maleic acid has been checked by absorption (73 ppm and 74 ppm). Moreover, number average molecular weight was about 2600 by GPC analysis. It is presumed that the matter expressed with a structure expression according to claim 1 by

the above thing was obtained.

[0033] The polyethylene-glycol 100 section of a mean molecular weight 8000 and the anhydrous methyl hexahydrophthalic acid 4.1 section were added to the 4 Thu openings flask of 1L equipped with example 2 thermometer, the capacitor, and the agitator, and the polyester resin which heats at 120 degrees C, is made to continue a reaction for 3 hours, and has two or more carboxyl groups in a molecule was obtained. Subsequently, the triphenyl phosphine 0.2 section was added as the bisphenol mold epoxy resin 12.3 section and a catalyst with weight per epoxy equivalent 190, the reaction was performed at 120 degrees C for 4 hours, and the resultant was taken out.

[0034] The equivalent ratio of a polyethylene glycol / anhydrous methyl hexahydrophthalic acid / epoxy resin is 1/2/2.6. Structural analysis of a product was performed like the example 1. In the infrared absorption spectrum, when characteristic absorption was in  $1720\text{cm}^{-1}$ , existence of ester has been checked. In NMR, existence of the ester of a polyethylene glycol and hexahydrophthalic acid has been checked by absorption (64 ppm and 68 ppm). Existence of the ester of an epoxy resin and a maleic acid has been checked by absorption (73 ppm and 74 ppm). Moreover, number average molecular weight was about 4000 by GPC analysis. It is presumed that the matter expressed with a structure expression according to claim 1 by the above thing was obtained.

[0035] The polyethylene-glycol 100 section of a mean molecular weight 3000 and the maleic-anhydride 4.9 section were added to the 4 Thu openings flask of 1L equipped with example 3 thermometer, the capacitor, and the agitator, and the polyester resin which heats at 120 degrees C, is made to continue the reaction during a tertiary stage, and has two or more carboxyl groups in a molecule was obtained. Subsequently, the triethylamine 0.5 section was added as the bisphenol A mold epoxy resin 14.6 section and a catalyst with weight per epoxy equivalent 190, the reaction was performed at 120 degrees C for 4 hours, and the resultant was taken out.

[0036] The equivalent ratio of a polyethylene glycol / maleic anhydride / epoxy resin is 1/1.5/1.2. Structural analysis of a product was performed like the example 1. In the infrared absorption spectrum, when characteristic absorption was in  $1720\text{cm}^{-1}$ , existence of ester has been checked. In NMR, existence of the ester of a polyethylene glycol and hexahydrophthalic acid has been checked by absorption (64 ppm and 68 ppm). Existence of the ester of an epoxy resin and a maleic acid has been checked by absorption (73 ppm and 74 ppm). Moreover, number average molecular weight was about 4000 by GPC analysis. It is presumed that the matter expressed with a structure expression according to claim 1 by the above thing was obtained.

[0037] As the polyethylene-glycol 100 section, the adipic-acid 19.1 section, and the catalyst of a mean molecular weight 8000, added the caustic soda 1 section, the reaction was made to continue at 200 degrees C for 2 hours in the 4 Thu openings flask of 1L equipped with example 4 thermometer, the capacitor, and the agitator, and polyester resin was obtained in it. Subsequently, temperature was lowered to 120 degrees C, the bisphenol A mold epoxy resin 25.1 section with weight per epoxy equivalent 190 was added, the reaction was performed at 120 degrees C for 4 hours, and the resultant was taken out.

[0038] The equivalent ratio of a polyethylene glycol / adipic acid / epoxy resin is 2. [ 1/ ]/2.6. Structural analysis of a product was performed like the example 1. In the infrared absorption spectrum, when characteristic absorption was in  $1720\text{cm}^{-1}$ , existence of ester has been checked. In NMR, existence of the ester of a polyethylene glycol and hexahydrophthalic acid has been checked by absorption (64 ppm and 68 ppm). Existence of the ester of an epoxy resin and a maleic acid has been checked by absorption (73 ppm and 74 ppm). Moreover, number average molecular weight was about 4400 by GPC analysis. It is presumed that the matter expressed with a structure expression according to claim 1 by the above thing was obtained.

[0039] By the 3-mil applicator, the mixture of the 50% water-solution 100 section of the epoxy resin obtained in the application 1 example 1 and the polyamide amine system curing agent 100 commercial section was applied to the glass plate. 4 - 5 hours after, it was hard and tough chemical resistance and paint film excellent in especially the water resisting property were obtained.

[0040] By the 3-mil applicator, the mixture of the 50% water-solution 100 section of the epoxy resin obtained in the application 2 example 2 and the polyamide amine system curing agent 100 commercial section was applied to the glass plate. 4 - 5 hours after, it was hard and tough chemical resistance and paint film which was rich in especially the water resisting property were obtained.

[0041] The mixture of the 50% water-solution 100 section of the epoxy resin obtained in the application 3 example 4 and the polyamide amine system curing agent 100 commercial section was applied to the glass plate in 3-mil PUPURIKE-TA -. 4 - 5 hours after, it was hard and tough chemical resistance and paint film which was rich in especially the water resisting property were obtained.

[0042]

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DESCRIPTION OF DRAWINGS

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[Brief Description of the Drawings]

[Drawing 1] It is the  $^{13}\text{C}$ -nuclear-magnetic-resonance spectrum of the epoxy resin obtained in the example 1.

[Drawing 2] It is the infrared absorption spectrum obtained in the example 1.

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[Translation done.]

[Effect of the Invention] Aquosity-izing is possible for the epoxy resin of this invention, and by using together with curing agents, such as a polyamide amine system, especially a water resisting property can obtain a good paint film, and this water solution comes, and is used in a coating, the adhesives field, etc.

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[Translation done.]



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(43)公開日 平成7年(1995)11月28日

### 技術表示箇所

審査請求 未請求 請求項の数 5 O L (全 6 頁)

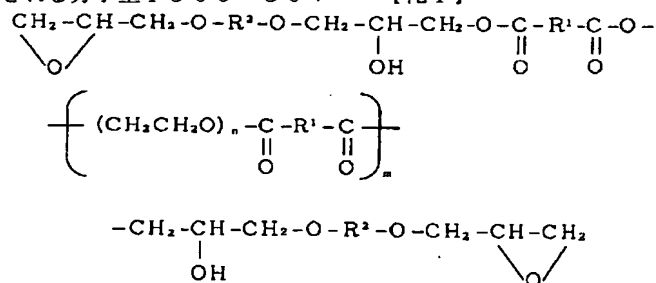
(74) 代理人 弁理士 高橋 勝利

(54) 【発明の名称】 エポキシ樹脂及びその製造方法

(57) 【要約】

\* 000のエポキシ樹脂及びその製造方法に関する。

【構成】下記の構造式で表される分子量1500~50\* 【化1】



〔式中、 $R^1$ は炭素数2～10の直鎖、分岐、または環状のカルボン酸を表す。また、 $R^1$ は $C_6H_4$ 、 $C(R^3)$ 、 $C_6H_3$ を示す。ここに $R^3$ はHまたは $CH_3$ を示す。〕

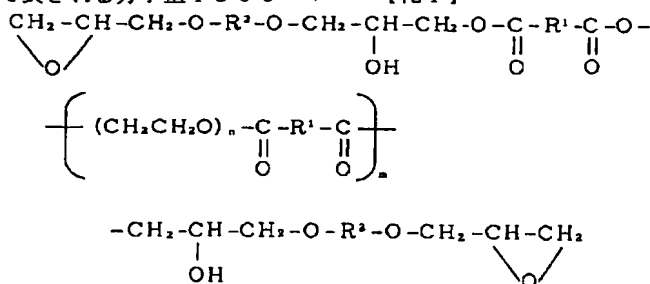
【効果】本発明のエポキシ樹脂は、水性化が可能であ

り、この水溶液はポリアミドアミン系等の硬化剤と併用することにより、特に耐水性が良好な塗膜を得ることができ、塗料、接着剤分野等で有用である。

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\* 50000のエポキシ樹脂。

【化1】



剤を添加して乳化分散させたエポキシ樹脂エマルジョンを作成し、これに硬化剤としてポリアミドポリアミン、芳香族アミンあるいはこれにエポキシアダクトを施した変性アミンなどのアミン系硬化剤を使用するのが一般的であった。

【０００６】このように界面活性剤を使用してエポキシ樹脂エマルジョンとする技術としては、特公昭４９－３４７３４号公報、特公昭５１－３３８２５号公報、特公昭５２－７８７号公報などに開示されている。

【０００７】しかしながら、上記の公報に開示されたエポキシ樹脂エマルジョンは、いずれも耐水性が悪く、使用の用途が限定される。すなわち、ポリアミドアミンと併用して塗工した場合、造膜後、塗膜上に水滴を落とすと、その部分が白化し跡が残り、美装塗膜が得られない。これは親水性の界面活性剤が塗膜中に硬化せずに分散した状態で存在するためと考えられる。

【０００８】また、親水性成分をエポキシ樹脂に導入する技術としては、特公昭６０－３１８５３号公報に開示されている。この技術は、平均分子量４０００あるいは６０００のポリエチレングリコールとエポキシ樹脂とを水酸基／エポキシ基の１／１当量比でエーテル化触媒の存在下で反応させて得られるエポキシ樹脂反応生成物を使用してエポキシ樹脂を乳化したものである。耐水性は上述の界面活性剤を使用した場合に比べてかなり向上するが、いまだ充分ではない。

【０００９】この理由は、得られるエポキシ樹脂反応生成物のエポキシ当量が１５０００以上となり、硬化に際して硬化剤との架橋が不十分であるためと推定される。

[ 0 0 1 0 ]

【発明が解決しようとする課題】本発明は、水性化可能で、耐水性に優れる新規なエポキシ樹脂及びその製造方法を提供することを目的とする。

[ 0 0 1 1 ]

【課題を解決するための手段】本発明者は、上記課題を解決するために鋭意研究を重ねた結果、分子内にポリオキシエチレン鎖を有する多価アルコールと多価カルボン酸またはその酸無水物とを反応させて得られる分子内に2個以上のカルボキシル基を有するポリエステル樹脂の

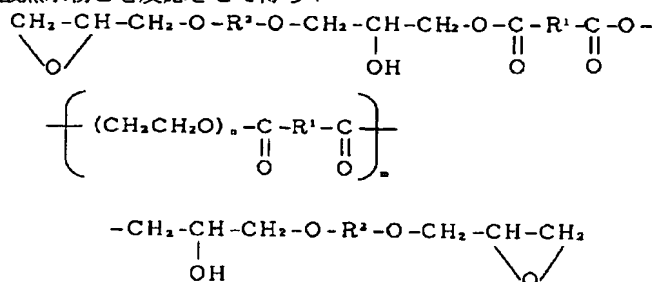
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\* れる分子内に２個以上のカルボキシル基を有するポリエステル樹脂と分子内に２個以上のエポキシ基を有するエポキシ樹脂とを反応させること特徴とする分子量１５００～５００００のエポキシ樹脂の製造方法に関する。

【 0 0 1 3 】

【化2】



【0018】上記繰り返し単位の繰り返し数 $m$ は1または2が好ましい。 $m$ が2よりも大きい場合にはいたずらに分子量が大きくなり、粘度が高くなり、取扱いが難しくなるので、好ましくない。

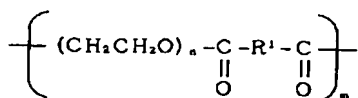
【００１９】本発明のエポキシ樹脂の分子量は１５００～５００００である。分子量が１５００より小さい場合は、繰返し単位のオキシエチレン鎖の $n$ の数を小さくせざるを得ず、水分散性が劣ったものとなる。一方、分子量が５００００より大きい場合には、エポキシ基の架橋密度を低下させることとなり、硬化後の耐水性などの物性が悪くなる。

【００２０】本発明のエポキシ樹脂は、例えば次の製造方法により得ることができる。すなわち、本発明のエポキシ樹脂は、分子内にポリオキシエチレン鎖を有する多価アルコールと多価カルボン酸またはその酸無水物とを反応（以下第一工程という）させて得られる分子内に２個以上のカルボキシル基を有するポリエステル樹脂と分子内に２個以上のエポキシ樹脂とを反応（以下第二工程という）させることにより得ることができる。

【0021】分子内にポリオキシエチレン鎖を有する多価アルコールの代表的なものはポリエチレングリコールであって、繰返し単位のおキシエチレン鎖の繰返し数nは20～500のものが好ましい。

40 【0022】多価カルボン酸またはその酸無水物は、直鎖、分岐、または環状の如何を問わない。多価カルボン酸としては、例えばマレイン酸、ヘキサヒドロフタル酸、こはく酸、フマル酸、アジピン酸、セバチン酸、イソフタル酸、テレフタル酸、メチルヘキサヒドロフタル酸、テトラヒドロフタル酸、メチルテオラヒドロフタル酸、エンドメチレンテトラヒドロフタル酸、メチルエンドメチレンテトラヒドロフタル酸及びその酸無水物などが挙げられる。

【0023】分子内に2個以上のエポキシ基を有するエポキシ樹脂とは、例えばビスフェノールAまたはビスフ



ェノールFとエピクロロヒドリンとを反応させて得られる従来より知られるエポキシ樹脂が挙げられる。

【0024】多価アルコールと多価カルボン酸またはその酸無水物よりポリエステル樹脂を得る第一工程の反応で、酸成分として多価カルボン酸を使用する場合には、多価アルコールの水酸基の1当量に対して多価カルボン酸のカルボキシル基を1.5～2.2当量にするのが好ましい。酸成分として酸無水物を使用する場合には、1個の酸無水物基は2個のカルボキシル基に相当する。

【0025】カルボキシル基が1.5当量よりも小さい場合には、得られるエポキシ樹脂が必要以上に高分子化して系の粘度が上昇するので好ましくない。また2.2当量より大きい場合には、第二工程において末端エポキシ基の割合が少なくなるので好ましくない。

【0026】第一工程の反応条件は通常のエステル化反応の場合に準じる。反応温度は250℃以下であり、酸成分として多価カルボン酸を使用する場合には、反応触媒は必要に応じて酸性触媒またはアルカリ性触媒を使用するのが好ましい。酸成分として酸無水物を使用すれば、100℃前後の低温で、無触媒または微量の触媒の使用で反応させることが可能であり、さらに、この場合高分子量化も防止することができる。

【0027】分子内にカルボキシル基を有するポリエステル樹脂と分子内に2個以上のエポキシ基を有するエポキシ樹脂との第二工程の反応は、ポリエステル樹脂のカルボキシル基の1当量に対してエポキシ樹脂のエポキシ基の1当量以上を反応させる必要がある。本発明のエポキシ樹脂の高分子量化を防ぐためには、上記分子内に2個以上のエポキシ基を有するエポキシ樹脂のエポキシ基を1.5当量以上とするのが好ましい。

【0028】第二工程の反応温度は100℃～150℃が好ましく、反応に際し、アルカリ触媒を使用することが好ましい。アルカリ触媒としては、例えば水酸化ナトリウム、および水酸化カリウムなどの水酸化物、トリエチルアミン、2-エチル4-メチルイミダゾールおよびベンジルジメチルアミンなどのアミン化合物、あるいはトリフェニルホスフィンなどを挙げることができる。

【0029】本発明のエポキシ樹脂は、水溶性であり、硬化剤と併用して硬化して得られる硬化塗膜は耐水性に優れるため、各種塗料、接着剤等の被覆用組成物に利用することができる。

【0030】

【実施例】以下、実施例を挙げて本発明の説明をするが、本発明はこれらの実施例に限定されるものではない。なお、実施例中の「部」は重量部を示す。

【0031】実施例1

温度計、コンデンサー、攪拌機を備えた1Lの4ツ口フラスコに平均分子量3000のポリエチレングリコール43.1部、平均分子量8000のポリエチレングリコール56.1部及び無水マレイン酸4.2部を加え、1

20℃に加熱し3時間反応を継続し、分子中に2個以上のカルボキシル基を有するポリエステル樹脂を得た。次いでエポキシ当量190を持つビスフェノールA型エポキシ樹脂20.9部、及び触媒としてトリフェニルホスフィン0.2部を加え、120℃で4時間反応を行い、反応生成物を取り出した。

【0032】ポリエチレングリコール／無水マレイン酸／エポキシ樹脂の当量比は1/2/2.6である。生成物の赤外線吸収スペクトル及び<sup>13</sup>C-NMR分析を行い構造解析を行った。赤外線吸収スペクトルでは、1720cm<sup>-1</sup>に特性吸収があることによりエステルの存在が確認出来た。NMRでは、64ppmおよび68ppmの吸収により、ポリエチレングリコールとマレイン酸のエステルの存在が確認出来た。73ppmと74ppmの吸収によりエポキシ樹脂とマレイン酸のエステルの存在が確認できた。又、GPC分析により数平均分子量は約2600であった。以上のことにより請求項1記載の構造式で表わされる物質が得られたと推定される。

【0033】実施例2

温度計、コンデンサー、攪拌機を備えた1Lの4ツ口フラスコに平均分子量8000のポリエチレングリコール100部及び無水メチルヘキサヒドロフタル酸4.1部を加え、120℃に加熱し3時間反応を継続させて分子中に2個以上のカルボキシル基を有するポリエステル樹脂を得た。次いでエポキシ当量190を持つビスフェノール型エポキシ樹脂12.3部及び触媒としてトリフェニルホスフィン0.2部を加え120℃で4時間反応を行い、反応生成物を取り出した。

【0034】ポリエチレングリコール／無水メチルヘキサヒドロフタル酸／エポキシ樹脂の当量比は1/2/2.6である。実施例1と同様に生成物の構造解析を行った。赤外線吸収スペクトルでは、1720cm<sup>-1</sup>に特性吸収があることによりエステルの存在が確認できた。NMRでは、64ppmおよび68ppmの吸収により、ポリエチレングリコールとヘキサヒドロフタル酸のエステルの存在が確認できた。73ppmと74ppmの吸収によりエポキシ樹脂とマレイン酸のエステルの存在が確認できた。又、GPC分析により数平均分子量は約4000であった。以上のことにより請求項1記載の構造式で表わされる物質が得られたと推定される。

【0035】実施例3

温度計、コンデンサー、攪拌機を備えた1Lの4ツ口フラスコに平均分子量3000のポリエチレングリコール100部及び無水マレイン酸4.9部を加え、120℃に加熱し3期間反応を継続させて分子中に2個以上のカルボキシル基を有するポリエステル樹脂を得た。次いでエポキシ当量190を持つビスフェノールA型エポキシ樹脂14.6部及び触媒としてトリエチルアミン0.5部を加え、120℃で4時間反応を行い、反応生成物を取り出した。

【0036】ポリエチレングリコール／無水マレイン酸／エポキシ樹脂の当量比は1／1.5／1.2である。実施例1と同様に生成物の構造解析を行った。赤外線吸収スペクトルでは、 $1720\text{ cm}^{-1}$ に特性吸収があることによりエステルが存在が確認できた。NMRでは、 $64\text{ ppm}$ および $68\text{ ppm}$ の吸収により、ポリエチレングリコールとヘキサヒドロフタル酸のエステルの存在が確認できた。 $73\text{ ppm}$ と $74\text{ ppm}$ の吸収によりエポキシ樹脂とマレイン酸のエステルの存在が確認できた。又、GPC分析により数平均分子量は約4000であった。以上のことにより請求項1記載の構造式で表わされる物質が得られたと推定される。

#### 【0037】実施例4

温度計、コンデンサー、攪拌機を備えた1Lの4ツ口フラスコに平均分子量8000のポリエチレングリコール100部、アジピン酸19.1部及び触媒として、カセイソーダ1部を加え $200^{\circ}\text{C}$ で2時間反応を継続させ、ポリエステル樹脂を得た。次いで $120^{\circ}\text{C}$ に温度を下げて、エポキシ当量190を持つビスフェノールA型エポキシ樹脂25.1部を加えて $120^{\circ}\text{C}$ で4時間反応を行

い、反応生成物を取り出した。  
【0038】ポリエチレングリコール／アジピン酸／エポキシ樹脂の当量比は1／2.／2.6である。実施例1と同様に生成物の構造解析を行った。赤外線吸収スペクトルでは、 $1720\text{ cm}^{-1}$ に特性吸収があることによりエステルが存在が確認できた。NMRでは、 $64\text{ ppm}$ および $68\text{ ppm}$ の吸収により、ポリエチレングリコールとヘキサヒドロフタル酸のエステルの存在が確認できた。 $73\text{ ppm}$ と $74\text{ ppm}$ の吸収によりエポキシ樹脂とマレイン酸のエステルの存在が確認できた。又、GPC分析により数平均分子量は約4400であった。以\*

\*上のことにより請求項1記載の構造式で表わされる物質が得られたと推定される。

#### 【0039】応用例1

実施例1で得られたエポキシ樹脂の50%水溶液100部と市販のポリアミドアミン系硬化剤100部の混合物を3ミルのアブリケーターにて、ガラス板に塗布した。4～5時間後、硬く、靱性のある、耐薬品性、特に耐水性に優れた塗膜が得られた。

#### 【0040】応用例2

実施例2で得られたエポキシ樹脂の50%水溶液100部と市販のポリアミドアミン系硬化剤100部の混合物を3ミルのアブリケーターにて、ガラス板に塗布した。4～5時間後、硬く、靱性のある、耐薬品性、特に耐水性に富んだ塗膜が得られた。

#### 【0041】応用例3

実施例4で得られたエポキシ樹脂の50%水溶液100部と市販のポリアミドアミン系硬化剤100部の混合物を3ミルのアブリケーターにて、ガラス板に塗布した。4～5時間後、硬く、靱性のある、耐薬品性、特に耐水性に富んだ塗膜が得られた。

#### 【0042】

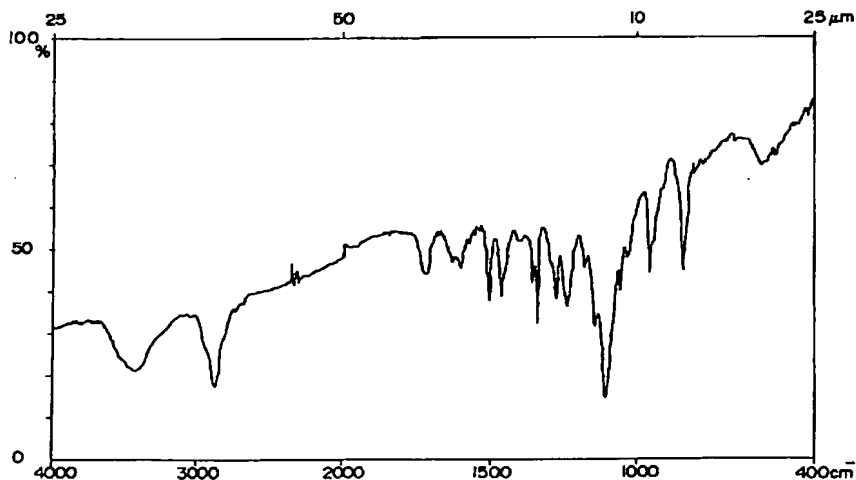
【発明の効果】本発明のエポキシ樹脂は、水性化が可能であり、この水溶液はポリアミドアミン系等の硬化剤と併用することにより、特に耐水性が良好な塗膜を得ることが出来き、塗料、接着剤分野等で利用される。

#### 【図面の簡単な説明】

【図1】実施例1で得られたエポキシ樹脂の $^{13}\text{C}$ -核磁気共鳴スペクトルである。

【図2】実施例1で得られた赤外線吸収スペクトルである。

【図1】



(6)

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【図2】

